

WO0015555

Title:
**METHODS TO PARTIALLY REDUCE A NIOBIUM METAL OXIDE AND
OXYGEN REDUCED NIOBIUM OXIDES**

Abstract:

Methods to at least partially reduce a niobium oxide are described wherein the process includes heat treating the niobium oxide in the presence of a getter material and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material, and for a sufficient time and at a sufficient temperature to form an oxygen reduced niobium oxide. Niobium oxides and/or suboxides are also described as well as capacitors containing anodes made from the niobium oxides and suboxides.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C01G 1/02, 35/00, 33/00, H01G 9/05, C04B 35/495	A1	(11) International Publication Number: WO 00/15555 (43) International Publication Date: 23 March 2000 (23.03.00)
(21) International Application Number: PCT/US99/21193 (22) International Filing Date: 15 September 1999 (15.09.99) (30) Priority Data: 09/154,452 16 September 1998 (16.09.98) US 09/347,990 6 July 1999 (06.07.99) US (71) Applicant: CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US). (72) Inventor: FIFE, James, A.; Apartment H, 642 East Flint Lake Court, Myrtle Beach, SC 29579 (US). (74) Agent: FINNEGAN, Martha, Ann; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHODS TO PARTIALLY REDUCE A NIOBIUM METAL OXIDE AND OXYGEN REDUCED NIOBIUM OXIDES (57) Abstract Methods to at least partially reduce a niobium oxide are described wherein the process includes heat treating the niobium oxide in the presence of a getter material and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material, and for a sufficient time and at a sufficient temperature to form an oxygen reduced niobium oxide. Niobium oxides and/or suboxides are also described as well as capacitors containing anodes made from the niobium oxides and suboxides.		

Patent provided by Sughrue Mion, PLLC - <http://www.sughrue.com>**BEST AVAILABLE COPY**

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

METHODS TO PARTIALLY REDUCE A NIOBIUM METAL OXIDE AND OXYGEN REDUCED NIOBIUM OXIDES

BACKGROUND OF THE INVENTION

The present invention relates to niobium and oxides thereof and more particularly relates to niobium oxides and methods to at least partially reduce niobium oxide and further relates to oxygen reduced niobium.

5

SUMMARY OF THE PRESENT INVENTION

In accordance with the purposes of the present invention, as embodied and described herein, the present invention relates to a method to at least partially reduce a niobium oxide which includes the steps of heat treating the niobium oxide in the presence of a getter material and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material for a sufficient time and temperature to form an oxygen reduced niobium oxide.

The present invention also relates to oxygen reduced niobium oxides which preferably have beneficial properties, especially when formed into an electrolytic capacitor anode. For instance, a capacitor made from the oxygen reduced niobium oxide of the present invention can have a capacitance of up to about 200,000 CV/g or more. Further, electrolytic capacitor anodes made from the oxygen reduced niobium oxides of the present invention can have a low DC leakage. For instance, such a

15

-2-

capacitor can have a DC leakage of from about 0.5 nA/CV to about 5.0 nA/CV.

Accordingly, the present invention also relates to methods to increase capacitance and reduce DC leakage in capacitors made from niobium oxides, which involves partially reducing a niobium oxide by heat treating the niobium oxide in the presence of a getter material and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material, for a sufficient time and temperature to form an oxygen reduced niobium oxide, which when formed into a capacitor anode, has reduced DC leakage and/or increased capacitance.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1-11 are SEMs of various oxygen reduced niobium oxides of the present invention at various magnifications.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

In an embodiment of the present invention, the present invention relates to methods to at least partially reduce a niobium oxide. In general, the method includes the steps of heat treating a starting niobium oxide in the presence of a getter material in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material for a sufficient time and at a sufficient temperature to form an oxygen reduced niobium oxide.

For purposes of the present invention, the niobium oxide can be at least one oxide of niobium metal and/or alloys thereof. A specific example of a starting niobium oxide is Nb_2O_5 .

The niobium oxide used in the present invention can be in any shape or size. Preferably, the niobium oxide is in the form of a powder or a plurality of particles. Examples of the type of powder that can be used include, but are not limited to, flaked, angular, nodular, and mixtures or variations thereof. Preferably, the niobium oxide is in the form of a powder which more effectively leads to the oxygen reduced niobium oxide.

Examples of such preferred niobium oxide powders include those having mesh sizes of from about 60/100 to about 100/325 mesh and from about 60/100 to about 200/325 mesh. Another range of size is from -40 mesh to about -325 mesh. In other words, the preferred niobium oxide powders have particle sizes from about 150/250 to about 45/150 microns, and from about 150/250 to about 45/75 microns. Another preferred size range is from about 355 microns to about 45 microns.

The getter material for purposes of the present invention is any material capable of reducing the specific starting niobium oxide to the oxygen reduced niobium oxide. Preferably, the getter material comprises tantalum, niobium, or both. Other examples include, but are not limited to, magnesium and the like. Any getter material that has a greater affinity for oxygen than niobium oxide can be used. More preferably, the getter material is niobium. The niobium getter material for purposes of the present invention is any material containing niobium metal which can remove or reduce at least partially the oxygen in the niobium oxide. Thus, the niobium getter material can be an alloy or a

-4-

material containing mixtures of niobium metal with other ingredients. Preferably, the niobium getter material is predominantly, if not exclusively, niobium metal. The purity of the niobium getter material is not important but it is preferred that high purity niobium comprise the getter material to avoid the introduction of other impurities during the heat treating process. Accordingly, the niobium metal in the niobium getter material preferably has a purity of at least about 98% and more preferably at least about 99%. Oxygen levels in the niobium getter material can be any amount. Preferably, impurities that affect DC leakage, such as iron, nickel, chromium, and carbon, are below about 100 ppm. Most preferably, the getter material is a niobium flake metal preferably having a high capacitance capability, such as greater than about 75,000 Cv/g and more preferably about 100,000 Cv/g or higher, such as about 200,000 Cv/g. The getter material also preferably has a high surface area, such as a BET of from about 5 to about 30 m²/g and more preferably from about 20 to about 30 m²/g.

The getter material can be in any shape or size. For instance, the getter material can be in the form of a tray which contains the niobium oxide to be reduced or can be in a particle or powder size. Preferably, the getter materials are in the form of a powder in order to have the most efficient surface area for reducing the niobium oxide. The getter material, thus, can be flaked, angular, nodular, and mixtures or variations thereof, e.g., coarse chips, such as 14/40 mesh chips that can be easily separated from the powder product by screening.

Similarly, the getter material can be tantalum and the like and can have the same preferred parameters and/or properties discussed above for the niobium getter material. Other getter materials can be used alone or in combination with the tantalum or niobium getter materials. Also, other materials can form a part of the getter material.

The getter material can be removed after being used or can remain. Preferably, if the getter material is to remain with the oxygen-reduced niobium oxides, then preferably the getter material is niobium, preferably having a similar shape and size to the starting niobium oxide. Further, preferably high purity, high surface area, and/or high porosity getter material (e.g., capacitor grade material) is used since such material will obtain the same or similar oxide state as the oxygen-reduced niobium oxide and thus the method will achieve a 100% yield of oxygen-reduced niobium oxide. Thus, the getter material can act as the getter material and also remain to become part of the oxygen-reduced niobium oxide.

Generally, a sufficient amount of getter material is present to at least partially reduce the niobium oxide being heat treated. Further, the amount of the getter material is dependent upon the amount of reducing desired to the niobium oxide. For instance, if a slight reduction in the niobium oxide is desired, then the getter material will be present in a stoichiometric amount. Similarly, if the niobium oxide is to be reduced substantially with respect to its oxygen presence, then the getter material is present in a 2 to 5 times stoichiometric amount. Generally, the amount of getter material present (e.g., based on the tantalum getter material being 100% tantalum) can be present based on the following ratio of getter material to the amount of niobium oxide present of from about 2 to 1 to about 10 to 1. The getter material is preferably blended or mixed together with the starting niobium oxide in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material (e.g., a hydrogen atmosphere), and preferably at a temperature of from about 1100°C to about 1500°C.

Furthermore, the amount of getter material can also be dependent on the type of

-6-

niobium oxide being reduced. For instance, when the niobium oxide being reduced is Nb_2O_5 , the amount of getter material is preferably 5 to 1. Also, when starting with Nb_2O_5 , a stoichiometric amount of getter material, preferably niobium flake metal, is used to achieve an oxide which preferably is 0.89 parts metal to 1 part oxide.

5 The heat treating that the starting niobium oxide is subjected to can be conducted in any heat treatment device or furnace commonly used in the heat treatment of metals, such as niobium and tantalum. The heat treatment of the niobium oxide in the presence of the getter material is at a sufficient temperature and for a sufficient time to form an oxygen reduced niobium oxide. The temperature and time of the heat
10 treatment can be dependent on a variety of factors such as the amount of reduction of the niobium oxide, the amount of the getter material, and the type of getter material as well as the type of starting niobium oxide. Generally, the heat treatment of the niobium oxide will be at a temperature of from less than or about 800°C to about 1900°C and more preferably from about 1000°C to about 1400°C, and most preferably from about
15 1100°C to about 1250°C. In more detail, the heat treatment temperatures will be from about 1000°C to about 1300°C, and more preferably from about 1100°C to about 1250°C for a time of from about 5 minutes to about 100 minutes, and more preferably from about 30 minutes to about 60 minutes. Routine testing in view of the present application will permit one skilled in the art to readily control the times and
20 temperatures of the heat treatment in order to obtain the proper or desired reduction of the niobium oxide.

The heat treatment occurs in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material. The heat treatment

-7-

preferably occurs in a hydrogen containing atmosphere which is preferably just hydrogen. Other gases can also be present with the hydrogen, such as inert gases, so long as the other gases do not react with the hydrogen. Preferably, the hydrogen atmosphere is present during the heat treatment at a pressure of from about 10 Torr to about 2000 Torr, and more preferably from about 100 Torr to about 1000 Torr, and most preferably from about 100 Torr to about 930 Torr. Mixtures of H_2 and an inert gas such as Ar can be used. Also, H_2 in N_2 can be used to effect control of the N_2 level of the niobium oxide.

During the heat treatment process, a constant heat treatment temperature can be used during the entire heat treating process or variations in temperature or temperature steps can be used. For instance, hydrogen can be initially admitted at $1000^\circ C$ followed by increasing the temperature to $1250^\circ C$ for 30 minutes followed by reducing the temperature to $1000^\circ C$ and held there until removal of the H_2 gas. After the H_2 or other atmosphere is removed, the furnace temperature can be dropped. Variations of these steps can be used to suit any preferences of the industry. The oxygen reduced niobium oxides can be subsequently reduced in size such as by crushing. The oxygen reduced niobium oxides can be agglomerated and crushed or processed in any other way that valve metals can be processed.

The oxygen reduced niobium oxides can also contain levels of nitrogen, e.g., from about 100 ppm to about 30,000 ppm N_2 .

The oxygen reduced niobium oxide is any niobium oxide which has a lower oxygen content in the metal oxide compared to the starting niobium oxide. Typical reduced niobium oxides comprise NbO , $NbO_{0.7}$, $NbO_{1.1}$, NbO_2 , and any combination

thereof with or without other oxides present. Generally, the reduced niobium oxide of the present invention has an atomic ratio of niobium to oxygen of about 1:less than 2.5, and preferably 1:2 and more preferably 1:1.1, 1:1, or 1:0.7. Put another way, the reduced niobium oxide preferably has the formula Nb_xO_y , wherein Nb is niobium, x is 5 2 or less, and y is less than 2.5x. More preferably x is 1 and y is less than 2, such as 1.1, 1.0, 0.7, and the like.

The starting niobium oxides can be prepared by calcining at 1000°C until removal of any volatile components. The oxides can be sized by screening. Preheat treatment of the niobium oxides can be used to create controlled porosity in the oxide 10 particles.

The reduced niobium oxides of the present invention also preferably have a microporous surface and preferably have a sponge-like structure, wherein the primary particles are preferably 1 micron or less. The SEMs further depict the type of preferred reduced niobium oxide of the present invention. As can be seen in these 15 microphotographs, the reduced niobium oxides of the present invention can have high specific surface area, and a porous structure with approximately 50% porosity. Further, the reduced niobium oxides of the present invention can be characterized as having a preferred specific surface area of from about 0.5 to about 10.0 m²/g, more preferably from about 0.5 to 2.0 m²/g, and even more preferably from about 1.0 to about 1.5 m²/g. 20 The preferred apparent density of the powder of the niobium oxides is less than about 2.0 g/cc, more preferably, less than 1.5 g/cc and even more preferably, from about 0.5 to about 1.5 g/cc. Also, the powder of the niobium oxides can have Scott densities, such as from about 5 g/in³ to about 35 g/in³.

-9-

The present invention has the ability to obtain properties similar to, if not better than, niobium and yet use less niobium in the product since an oxygen-reduced niobium oxide is formed and used. Thus, the present invention extends the amount of niobium in products, such as capacitor anodes, since more anodes or other products can be
5 manufactured using the same amount of niobium.

The various oxygen reduced niobium oxides of the present invention can be further characterized by the electrical properties resulting from the formation of a capacitor anode using the oxygen reduced niobium oxides of the present invention. In general, the oxygen reduced niobium oxides of the present invention can be tested for
10 electrical properties by pressing powders of the oxygen reduced niobium oxide into an anode and sintering the pressed powder at appropriate temperatures and then anodizing the anode to produce an electrolytic capacitor anode which can then be subsequently tested for electrical properties.

Accordingly, another embodiment of the present invention relates to anodes for
15 capacitors formed from the oxygen reduced niobium oxides of the present invention. Anodes can be made from the powdered form of the reduced oxides in a similar process as used for fabricating metal anodes, i.e., pressing porous pellets with embedded lead wires or other connectors followed by optional sintering and anodizing. The lead connector can be embedded or attached at any time before anodizing. Anodes made
20 from some of the oxygen reduced niobium oxides of the present invention can have a capacitance of from about 1,000 CV/g or lower to about 300,000 CV/g or more, and other ranges of capacitance can be from about 20,000 CV/g to about 300,000 CV/g or from about 62,000 CV/g to about 200,000 CV/g and preferably from about 60,000 to 150,000 CV/g. In forming the capacitor anodes of the present invention, a sintering

-10-

temperature can be used which will permit the formation of a capacitor anode having the desired properties. The sintering temperature will be based on the oxygen reduced niobium oxide used. Preferably, the sintering temperature is from about 1200°C to about 1750°C and more preferably from about 1200°C to about 1400°C and most preferably from about 1250°C to about 1350°C when the oxygen reduced niobium oxide is an oxygen reduced niobium oxide.

The anodes formed from the niobium oxides of the present invention are preferably formed at a voltage of about 35 volts and preferably from about 6 to about 70 volts. When an oxygen reduced niobium oxide is used, preferably, the forming voltages are from about 6 to about 50 volts, and more preferably from about 10 to about 40 volts. Other high formation voltages can be used. Anodes of the reduced niobium oxides can be prepared by fabricating a pellet of Nb_2O_5 with a lead wire followed by sintering in H_2 atmosphere or other suitable atmosphere in the proximity of a getter material just as with powdered oxides. In this embodiment, the anode article produced can be produced directly, e.g., forming the oxygen reduced valve metal oxide and an anode at the same time. Also, the anodes formed from the oxygen reduced niobium oxides of the present invention preferably have a DC leakage of less than about 5.0 nA/CV. In an embodiment of the present invention, the anodes formed from some of the oxygen reduced niobium oxides of the present invention have a DC leakage of from about 5.0 nA/CV to about 0.50 nA/CV.

The present invention also relates to a capacitor in accordance with the present invention having a niobium oxide film on the surface of the capacitor. Preferably, the film is a niobium pentoxide film. The means of making metal powder into capacitor

-11-

anodes is known to those skilled in the art and such methods such as those set forth in U.S. Pat. Nos. 4,805,074, 5,412,533, 5,211,741, and 5,245,514, and European Application Nos. 0 634 762 A1 and 0 634 761 A1, all of which are incorporated in their entirety herein by reference.

5 The capacitors of the present invention can be used in a variety of end uses such as automotive electronics, cellular phones, computers, such as monitors, mother boards, and the like, consumer electronics including TVs and CRTs, printers/copiers, power supplies, modems, computer notebooks, disc drives, and the like.

 The present invention will be further clarified by the following examples, which
10 are intended to be exemplary of the present invention.

TEST METHODS

Anode Fabrication:

15 size - 0.197" dia
 3.5 Dp
 powder wt = 341 mg

Anode Sintering:

20 1300 Deg C* 10'
 1450 Deg C* 10'
 1600 Deg C* 10'
 1750 Deg C* 10'

30V Ef Anodization:

25 30V Ef @ 60 Deg C/0.1% H3PO4 Electrolyte
 20 mA/g constant current

DC Leakage/Capacitance - ESR Testing:

30 DC Leakage Testing ---
 70% Ef (21 VDC) Test Voltage
 60 second charge time
 10% H3PO4 @ 21 Deg C
 Capacitance - DF Testing:
35 18% H2SO4 @ 21 Deg C
 120Hz

-12-

50V Ef Reform Anodization:

50V Ef @ 60 Deg C/0.1% H₃PO₄ Electrolyte
20 mA/g constant current

5

DC Leakage/Capacitance - ESR Testing:

DC leakage Testing ---

70% Ef (35 VDC) Test Voltage

60 second charge time

10

10% H₃PO₄ @ 21 Deg C

Capacitance - DF Testing:

18% H₂SO₄ @ 21 Deg C

120Hz

15

75V Ef Reform Anodization:

75V Ef @ 60 Deg C/0.1% H₃PO₄ Electrolyte
20 mA/g constant current

DC Leakage/Capacitance - ESR Testing:

20

DC leakage Testing ---

70% Ef (52.5 VDC) Test Voltage

60 second charge time

10% H₃PO₄ @ 21 Deg C

Capacitance - DF Testing:

25

18% H₂SO₄ @ 21 Deg C

120 Hz

Scott Density, oxygen analysis, phosphorus analysis, and BET analysis were determined according to the procedures set forth in U.S. Patent Nos. 5,011,742; 4,960,471; and 4,964,906, all incorporated hereby in their entireties by reference herein.

EXAMPLES

Example 1

35 +10 mesh Ta hydride chips (99.2 gms) with approximately 50 ppm oxygen were mixed with 22 grams of Nb₂O₅ and placed into Ta trays. The trays were placed into a

-13-

vacuum heat treatment furnace and heated to 1000°C. H₂ gas was admitted to the furnace to a pressure of +3psi. The temperature was further ramped to 1240°C and held for 30 minutes. The temperature was lowered to 1050°C for 6 minutes until all H₂ was swept from the furnace. While still holding 1050°C, the argon gas was evacuated from
5 the furnace until a pressure of 5×10^{-4} torr was achieved. At this point 700 mm of argon was readmitted to the chamber and the furnace cooled to 60°C.

The material was passivated with several cyclic exposures to progressively higher partial pressures of oxygen prior to removal from the furnace as follows: The furnace was backfilled with argon to 700 mm followed by filling to one atmosphere
10 with air. After 4 minutes the chamber was evacuated to 10^{-2} torr. The chamber was then backfilled to 600 mm with argon followed by air to one atmosphere and held for 4 minutes. The chamber was evacuated to 10^{-2} torr. The chamber was then backfilled to 400 mm argon followed by air to one atmosphere. After 4 minutes the chamber was evacuated to 10^{-2} torr. The chamber was then backfilled to 200 mm argon followed by
15 air to one atmosphere and held for 4 minutes. The chamber was evacuated to 10^{-2} torr. The chamber was backfilled to one atmosphere with air and held for 4 minutes. The chamber was evacuated to 10^{-2} torr. The chamber was backfilled to one atmosphere with argon and opened to remove the sample.

The powder product was separated from the tantalum chip getter by screening
20 through a 40 mesh screen. The product was tested with the following results.

CV/g of pellets sintered to 1300°C X 10 minutes and formed to 35 volts = 81,297

-14-

nA/CV (DC leakage) = 5.0
 Sintered Density of pellets = 2.7 g/cc
 Scott density = 0.9 g/cc
 Chemical Analysis (ppm)
 C = 70
 H₂ = 56
 Ti = 25
 Mn = 10
 Sn = 5
 Cr = 10
 Mo = 25
 Cu = 50
 Pb = 2

Fe = 25
 Si = 25
 Ni = 5
 Al = 5
 Mg = 5
 B = 2
 all others < limits

Example 2

Samples 1 through 20 are examples following similar steps as above with powdered Nb₂O₅ as indicated in the Table. For most of the examples, mesh sizes of the starting input material are set forth in the Table, for example 60/100, means smaller than 60 mesh, but larger than 100 mesh. Similarly, the screen size of some of the Ta getter is given as 14/40. The getters marked as "Ta hydride chip" are +40 mesh with no upper limit on particle size.

Sample 18 used Nb as the getter material (commercially available N200 flaked Nb powder from CPM). The getter material for sample 18 was fine grained Nb powder which was not separated from the final product. X-ray diffraction showed that some of the getter material remained as Nb, but most was converted to NbO_{1.1} and NbO by the process as was the starting niobium oxide material Nb₂O₅.

Sample 15 was a pellet of Nb₂O₅, pressed to near solid density, and reacted with H₂ in close proximity to the Ta getter material. The process converted the solid oxide pellet into a porous slug of NbO suboxide. This slug was sintered to a sheet of Nb metal to create an anode lead connection and anodized to 35 volts using similar

-15-

electrical forming procedures as used for the powder slug pellets. This sample demonstrates the unique ability of this process to make a ready to anodize slug in a single step from Nb_2O_5 starting material.

The Table shows the high capacitance and low DC leakage capability of anodes
5 made from the pressed and sintered powders/pellets of the present invention.

Microphotographs (SEMs) of various samples were taken. These photographs show the porous structure of the reduced oxygen niobium oxide of the present invention. In particular, Figure 1 is a photograph of the outer surface of a pellet taken at 5,000 X (sample 15). Figure 2 is a photograph of the pellet interior of the same pellet taken at
10 5,000 X. Figures 3 and 4 are photographs of the outer surface of the same pellet at 1,000 X. Figure 5 is a photograph of sample 11 at 2,000 X and Figures 6 and 7 are photographs taken of sample 4 at 5,000 X. Figure 8 is a photograph taken of sample 3 at 2,000 X and Figure 9 is a photograph of sample 6 at 2,000 X. Finally, Figure 10 is a photograph of sample 6, taken at 3,000 X and Figure 11 is a photograph of sample 9
15 taken at 2,000 X.

TABLE

Sample	Input Material	Gms	Input Getter	Gms	Temp (°C)	Time (min)	Hydrogen Pressure	XRD* Major 1**	XRD* Major 2**	XRD* Minor 1***	XRD* Minor 2***	1300X35v CV/g	1300X35v na/CV
1	-40 mesh calcined Nb ₂ O ₅	20 (est)	Ta hydride chips	40 (est)	1240	30	3 psi					81297	5
2	60/100 Nb ₂ O ₅	23.4	Ta hydride chips	65.4	1250	30	3 psi	NbO _{1.1}	NbO	TaO		115379	1.28
3	60/100 Nb ₂ O ₅	23.4	Ta hydride chips	65.4	1250	30	3 psi	NbO _{1.1}	NbO	TaO		121293	2.19
4	100/325 Nb ₂ O ₅	32.3	Ta hydride chips	92.8	1250	30	3 psi					113067	1.02
5	100/325 Nb ₂ O ₅	32.3	Ta hydride chips	92.8	1250	30	3 psi					145589	1.42
6	60/100 Nb ₂ O ₅	26.124	Ta hydride chips	72.349	1250	90	3 psi					17793	12.86
7	60/100 Nb ₂ O ₅	26.124	Ta hydride chips	72.349	1250	90	3 psi					41525	5.63
8	200/325 Nb ₂ O ₅	29.496	Ta hydride chips	83.415	1250	90	3 psi					17790	16.77
9	60/100 Nb ₂ O ₅	20.888	Ta hydride chips	60.767	1200	90	3 psi	NbO _{1.1}	NbO	Ta ₂ O ₅		63257	5.17
10	60/100 Nb ₂ O ₅	20.888	Ta hydride chips	60.767	1200	90	3 psi	NbO _{1.1}	NbO	Ta ₂ O ₅		69881	5.5
11	200/325 Nb ₂ O ₅	23.936	Ta hydride chips	69.266	1200	90	3 psi	NbO _{1.1}	NbO	Ta ₂ O ₅		61716	6.65
12	200/325 Nb ₂ O ₅	23.936	Ta hydride chips	69.266	1200	90	3 psi	NbO _{1.1}	NbO	Ta ₂ O ₅		68245	6.84
13	200/325 Nb ₂ O ₅	15.5	14/40 Ta hydride	41.56	1250	30	3 psi	NbO _{0.7}	NbO	TaO	NbO ₂	76294	4.03
14	200/325 Nb ₂ O ₅	10.25	14/40 Ta hydride	68.96	1250	30	3 psi	NbO _{0.7}	NbO	TaO	NbO ₂	29281	21.03
15	Nb ₂ O ₅ pellets	3.49	14/40 Ta hydride	25.7	1250	30	3 psi					70840	0.97
16	200/325 Nb ₂ O ₅	13.2	14/40 Ta hydride	85.7	1200	30	3 psi	NbO ₂	NbO _{0.7}	TaO	NbO	5520	34.33
17	200/325 Nb ₂ O ₅	14.94	14/40 Ta hydride	41.37	1200	30	3 psi					6719	38.44
18	200/325 Nb ₂ O ₅	11.92	N200 Nb powder	21.07	1200	30	3 psi	Nb	NbO _{1.1}	NbO		25716	4.71
19	200/325 Nb ₂ O ₅	10	14/40 Ta hydride	69	1250	30	100 Torr					108478	1.95
20	200/325 Nb ₂ O ₅	16	14/40 Ta hydride	41	1250	30	100 Torr					106046	1.66

* X-Ray Diffraction Analysis Results

** Major 1 and 2 refer to primary components present by weight.

*** Minor 1 and 2 refer to secondary components present by weight.

5 Samples 11 and 12 had the same input material. Samples 2 and 3 had the same input material. Samples 6 and 7 had the same input material. Samples 9 and 10 had the same input material.

-17-

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following

5 claims.

WHAT IS CLAIMED IS:

1. A method to at least partially reduce a niobium oxide comprising heat treating the niobium oxide in the presence of a getter material and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material, for a sufficient time and temperature to form an oxygen reduced niobium oxide.
2. The method of claim 1, wherein the niobium oxide is a niobium pentoxide.
3. The method of claim 1, wherein the oxygen reduced niobium oxide is a niobium suboxide.
4. The method of claim 1, wherein the oxygen reduced niobium oxide has a niobium to oxygen atomic ratio of 1:less than 2.5.
5. The method of claim 1, wherein the oxygen reduced niobium oxide has oxygen levels that are less than stoichiometric for a fully oxidized niobium.
6. The method of claim 1, wherein the oxygen reduced niobium oxide has a micro-porous structure.
7. The method of claim 1, wherein the oxygen reduced niobium oxide has a pore volume of about 50%.
8. The method of claim 1, wherein the atmosphere is hydrogen present in an amount of about 10 Torr to about 2000 Torr.
9. The method of claim 1, wherein the getter material is a niobium getter material capable of a capacitance of at least 75,000 Cv/g when formed into an anode.

10. The method of claim 1, wherein the atmosphere is a hydrogen atmosphere.

11. The method of claim 1, wherein the getter material is a niobium getter material is capable of a capacitance of from about 100,000 Cv/g to about 200,000 Cv/g
5 when formed into an anode.

12. The method of claim 1, wherein said heat treating is at a temperature of from about 1000°C to about 1500°C and for about 10 to about 90 minutes.

13. The method of claim 1, wherein said getter material is homogenized with the niobium oxide prior to or during the heat treating step.

10 14. The method of claim 1, wherein the getter material is a niobium flaked getter material.

15. The method of claim 1, wherein the getter material, after heat treating, forms an oxygen reduced niobium oxide.

16. The method of claim 1, wherein the getter material is a magnesium
15 containing getter material.

17. The method of claim 1, wherein the getter material comprises tantalum hydride particles.

18. The method of claim 1, wherein the getter material comprises tantalum, niobium, or both.

20 19. The method of claim 1, wherein the getter material is 14/40 mesh tantalum hydride particles.

20. The method of claim 1, wherein said getter material is a capacitor grade material.

-20-

21. A niobium oxide having an atomic ratio of niobium to oxygen of 1:less than 2.5.
22. The niobium oxide of claim 21, wherein the atomic ratio is 1:less than 2.0.
- 5 23. The niobium oxide of claim 21, wherein the atomic ratio is 1:less than 1.5.
24. The niobium oxide of claim 21, wherein the atomic ratio is 1:1.1.
25. The niobium oxide of claim 21, wherein the atomic ratio is 1:0.7.
26. The niobium oxide of claim 21, wherein the atomic ratio is 1:0.5.
- 10 27. The niobium oxide of claim 21, wherein said niobium oxide has a porous structure.
28. The niobium oxide of claim 21, wherein said niobium oxide has a porous structure having from about .1 to about 10 micrometer pores.
29. The niobium oxide of claim 21, wherein said niobium oxide comprises
- 15 NbO , $\text{NbO}_{0.7}$, $\text{NbO}_{1.1}$, or combinations thereof.
30. The niobium oxide of claim 21, wherein said niobium oxide is formed into an electrolytic capacitor anode having a capacitance of up to about 300,000 CV/g.
31. The niobium oxide of claim 21, further comprising nitrogen.
32. The niobium oxide of claim 31, wherein said nitrogen is present in the
- 20 amount of from about 100 ppm to about 30,000 ppm N_2 .
33. The niobium oxide of claim 21, wherein said niobium oxide is formed into an electrolytic capacitor anode, said anode having a capacitance of from about 1,000 to about 300,000 CV/g.

-21-

34. The niobium oxide of claim 33, wherein said capacitance is from about 60,000 to about 200,000 CV/g.

35. The niobium oxide of claim 33, wherein said anode has a DC leakage of from about .5 to about 5 nA/CV.

5 36. The niobium oxide of claim 21, wherein said niobium comprises nodular, flaked, angular, or combinations thereof.

37. A capacitor comprising the niobium oxide of claim 21.

38. A capacitor comprising the niobium oxide of claim 33.

39. The niobium oxide of claim 21, wherein said niobium oxide is sintered
10 at a temperature of from about 1200°C to about 1750°C.

40. The niobium oxide of claim 21, wherein said niobium oxide is sintered at a temperature of from about 1200°C to about 1450°C.

41. The capacitor of claim 37, having a capacitance of from about 1,000 CV/g to about 300,000 CV/g.

15 42. The capacitor of claim 37, having a capacitance of from about 60,000 CV/g to about 200,000 CV/g.

43. The capacitor of claim 37, having a DC leakage of from about .5 to about 5 nA/CV.

44. A method of making a capacitor anode comprising a) fabricating a pellet
20 of niobium oxide and heat treating the pellet in the presence of a getter material, and in an atmosphere which permits the transfer of oxygen atoms from the niobium oxide to the getter material, and for a sufficient time and temperature to form an electrode body comprising the pellet, wherein the pellet comprises an oxygen reduced niobium oxide, and b) anodizing said electrode body to form said capacitor anode.

-22-

45. The method of claim 44, wherein the atmosphere is a hydrogen atmosphere.

46. The method of claim 44, wherein the getter material comprises tantalum, niobium, or both.

5 47. The method of claim 44, wherein the getter material is niobium.

48. The method of claim 44, wherein the oxygen reduced niobium oxide has an atomic ratio of niobium to oxygen of 1:less than 2.5.



FIG. 1

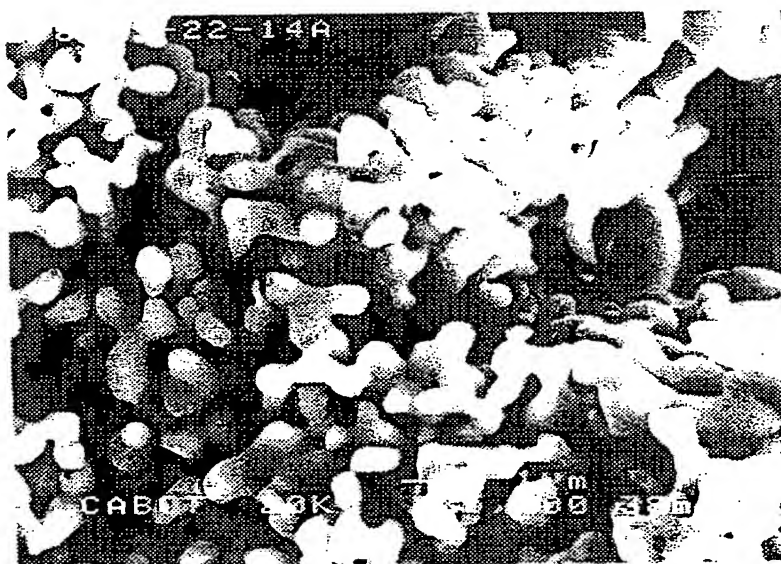


FIG. 2



FIG. 3

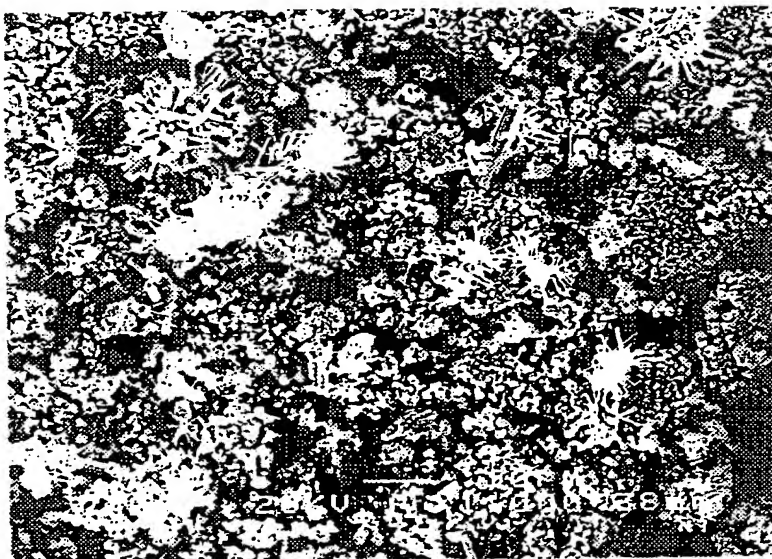


FIG. 4

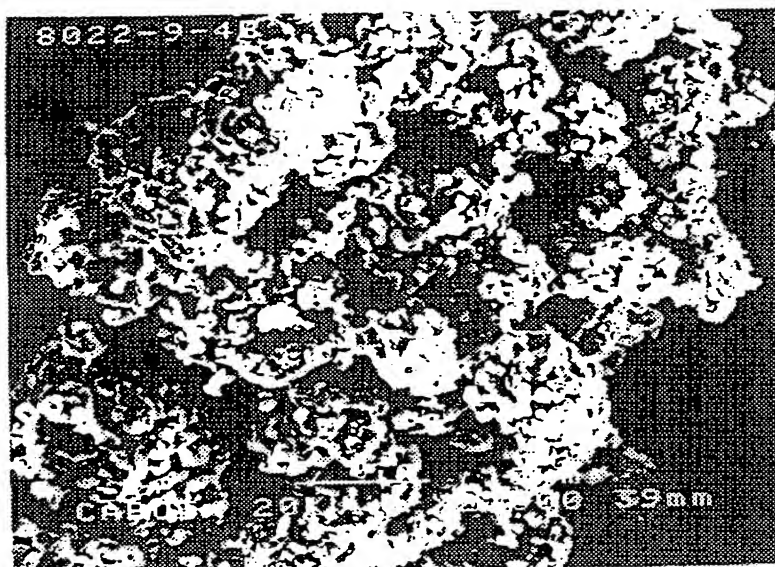


FIG. 5

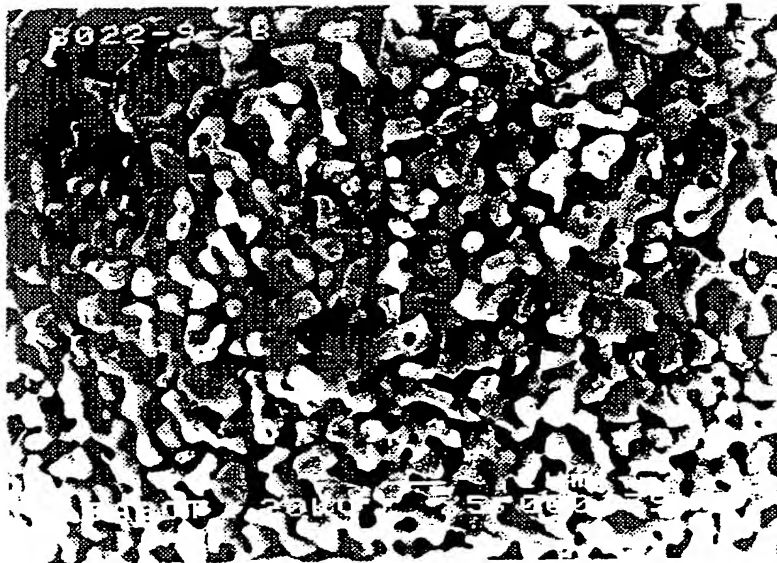


FIG. 6

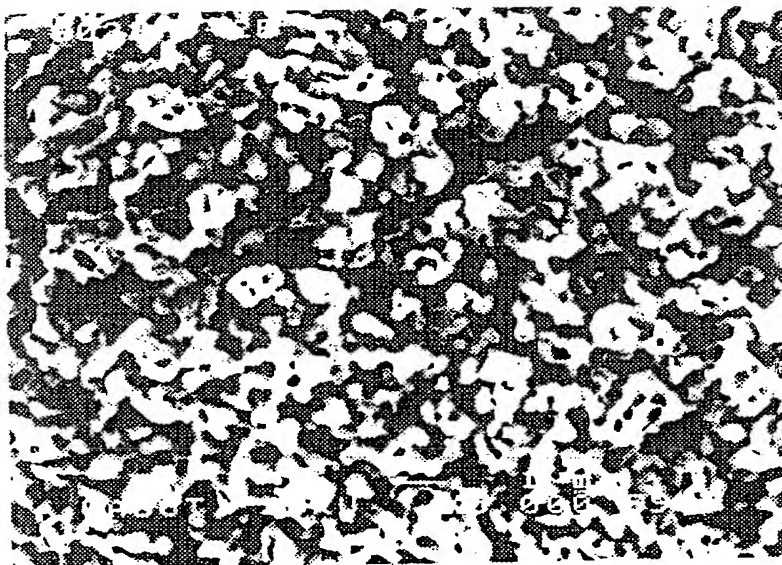


FIG. 7

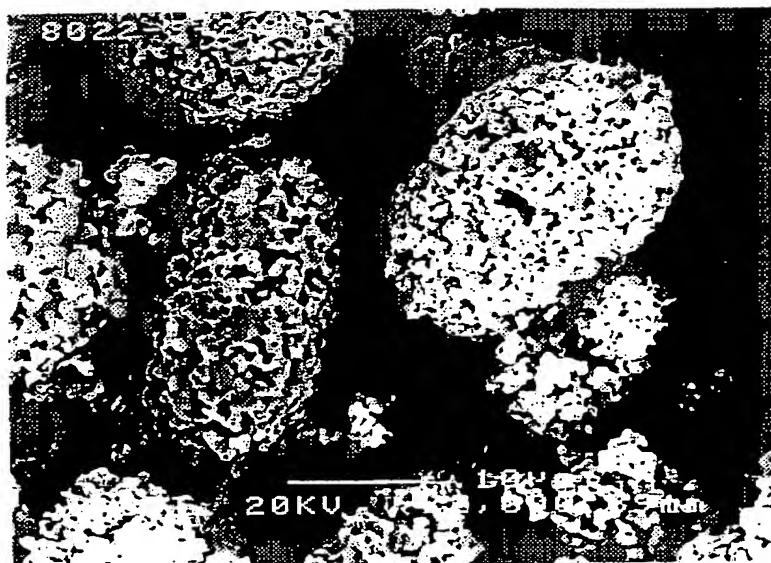


FIG. 8

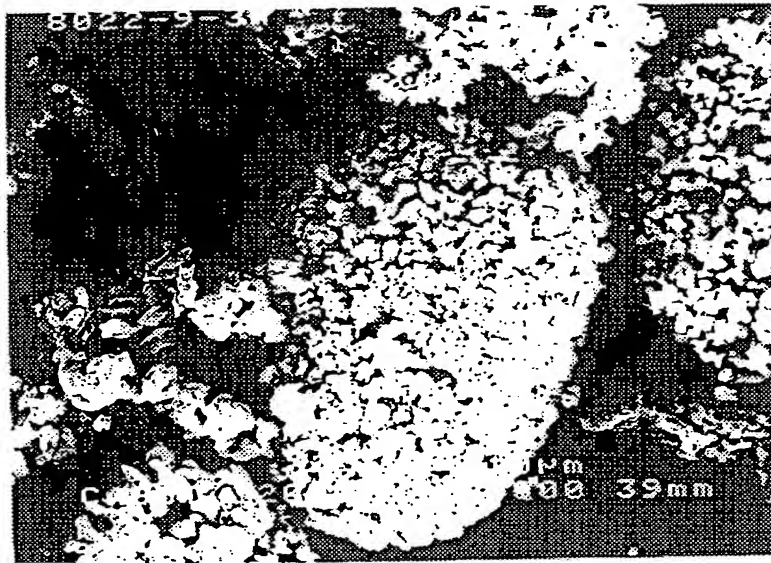


FIG. 9

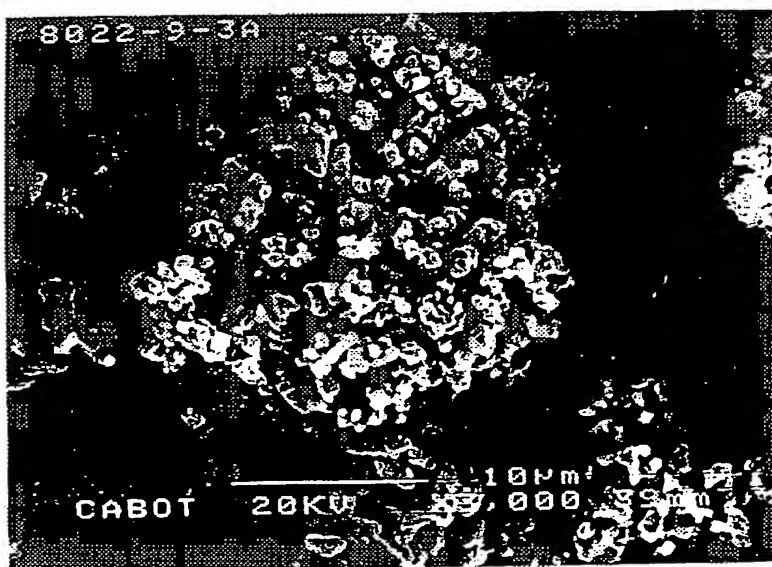


FIG. 10

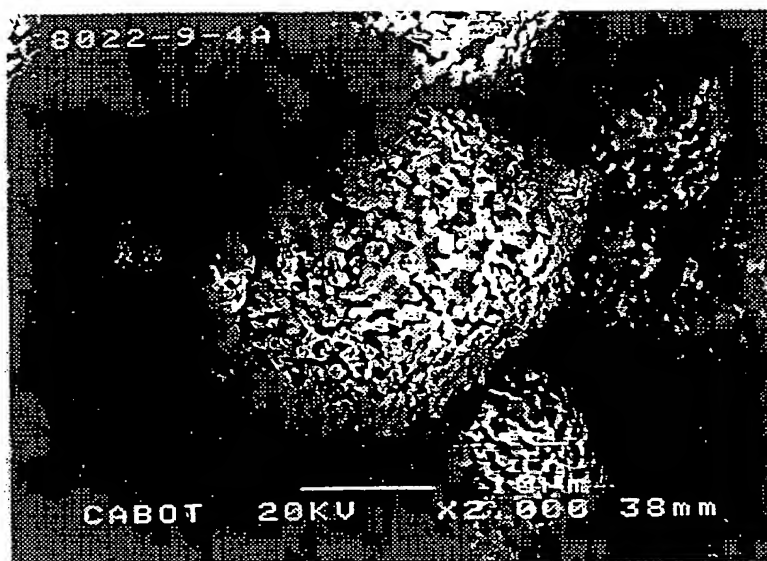


FIG. 11

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21193

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G1/02 C01G35/00 C01G33/00 H01G9/05 C04B35/495

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G H01G C03B C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 201 798 A (SOLAREX CORP.) 6 May 1980 (1980-05-06) column 3, line 40 - line 45 column 4, line 15 - line 20	21-23, 29
Y	---	37
Y	US 5 412 533 A (ROHM CO., LTD.) 2 May 1995 (1995-05-02) cited in the application the whole document	37
Y, P	US 5 825 611 A (VISHAY SPRAGUE, INC.) 20 October 1998 (1998-10-20) the whole document -----	37

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2000

Date of mailing of the international search report

17/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Luethe, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/21193

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4201798 A	06-05-1980	US 4156622 A	29-05-1979
US 5412533 A	02-05-1995	JP 2789074 B	20-08-1998
		JP 7086097 A	31-03-1995
		JP 7037761 A	07-02-1995
		DE 4421772 A	16-02-1995
US 5825611 A	20-10-1998	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.